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(54) METHOD FOR MANUFACTURING ACTINIC RAY-CURABLE RESIN AND ACTINIC RAY-CURABLE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing an actinic ray-curable resin capable of producing the resin with a reduced amount of a halogen catalyst or the like, or even with a non-halogen catalyst, and capable of producing the resin suitable for a resist, excellent in basic properties and having widely improved properties such as tenacity, and to provide an actinic ray-curable resin composition.

SOLUTION: The method for manufacturing an actinic ray-curable resin comprises reacting a hydroxy-containing modified epoxyacrylate compound (A) with an acid anhydride (B). The compound (A) is obtained by reacting a bifunctional epoxy resin (a1), a monocarboxylic acid (a2) having a (meth) acryloyl group and a dicarboxylic acid (a3) including a dicarboxylic acid having a (meth)acryloyl group with each other at specific ratios in the presence of a catalyst. Further, a resin composition containing the actinic ray-curable resin (I) and an epoxy compound (II).

LEGAL STATUS

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AN 2002:465593 CAPLUS
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 ED Entered STN: 21 Jun 2002
 TI Manufacture of energy ray-curable epoxy resin acrylates by using reduced amounts of or without using halogen-containing catalysts and their resin compositions for solder resists
 IN Ichinose, Hidetoshi; Yamashina, Hirozo; Ishikawa, Hidenobu
 PA Dainippon Ink and Chemicals, Inc., Japan
 SO Jpn. Kokai Tokkyo Koho, 16 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08G059-17
 ICS C08G059-58; C08G059-68
 CC 74-5 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
 Section cross-reference(s): 38
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PRAI	JP 2000-296512	A	20000928		

AB The energy ray-curable resins (I) are prepared by reacting (A) HO-containing modified epoxy acrylates prepared by a reaction catalyzed by, preferably nonhalogen or phosphine-based catalysts, (a1) bifunctional epoxy resins, (a2) monocarboxylic acids bearing (meth)acryloyl groups, and (a3) dicarboxylic acids involving those bearing (meth)acryloyl groups at a ratio satisfying $0.9na1 < na2 + na3 < 1.1na1$ and $0.2 < na2/na3 < 4.0$ ($na1$ = molar number of total epoxy groups in a1; $na2$, $na3$ = molar nos. of total CO₂H in a2 and a3, resp.) (and) (B) acid anhydrides. The compns. containing the resins I and epoxy compds. (II) show high sensitivity to UV, electron beam, etc., are developable with aqueous alkalis, offers cured films having high heat resistance, hardness, elongation, elec. properties, and are useful for permanent protection masks such as solder resists for printed circuits, etc.

ST energy ray curable epoxy resin acrylate; acid anhydride hydroxy epoxy acrylate reaction; solder resist vinyl ester resin curability; halogen free catalyst epoxy acrylate prepn; phosphine catalyzed epoxy acrylate prepn resist

IT Epoxy resins, preparation
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (acrylates, hydroxy-containing, reaction products with acid anhydrides, cured with epoxies; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT Epoxy resins, reactions
 RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
 (acrylates, hydroxy-containing, reaction products with acid anhydrides; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT Phenolic resins, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (epoxy, novolak; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT Solder resists
 (manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT Epoxy resins, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (phenolic, novolak; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT Solder resists

(photoresists; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT Photoresists
 (solder; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT 438210-71-0P 438210-72-1P 438210-73-2P 438210-74-3P 438238-74-5P
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (crosslinked; manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT 603-35-0, Triphenylphosphine, uses
 RL: CAT (Catalyst use); USES (Uses)
 (manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT 438210-64-1P 438210-66-3P 438210-67-4P 438210-69-6P 438210-70-9P
 RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
 (manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

IT 29570-58-9, Dipentaerythritol hexaacrylate 412044-75-8, EE 214
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (manufacture of energy ray-curable epoxy resin acrylates without using halogen-containing catalysts for solder resist compns.)

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DERWENT-WEEK: 200302

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TITLE: Process for producing an energy ray curable resin useful for resist, in which the amount of the halogen type catalyst is reduced

PATENT-ASSIGNEE: DAINIPPON INK & CHEM INC [DNIN]

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INT-CL (IPC): C08G059/17, C08G059/68, C08G059/68

ABSTRACTED-PUB-NO: JP2002173518A

BASIC-ABSTRACT:

NOVELTY - A process for producing an energy ray curable resin, in which (A) hydroxyl group containing modified epoxy acrylate compound and (B) an acid anhydride are reacted.

DETAILED DESCRIPTION - A process for producing an energy ray curable resin, in which (A) hydroxyl group containing modified epoxy acrylate compound (which is obtained by reacting (a1) a bifunctional epoxy resin, (a2) a (meth)acryloyl group containing monocarboxylic acid and (a3) a dicarboxylic acid (which contains a (meth)acryloyl group containing dicarboxylic acid) in the presence of a catalyst, at such a ratio that satisfy the following equations (1) and (2)), and (B) an acid anhydride are reacted.

0. $9 \text{ na1 less than na2} + \text{na3 less than } 1.1 \text{ na1}$ (1)

0.2 less than na2/na3 less than 4.0 (2)

(wherein, na1 refers to the total epoxy groups in the epoxy resin (a1) (unit:mol), na2 refers to the total carboxyl groups in the monocarboxylic acid (a2) (unit:mol) and na3 refers to the total carboxyl groups in the dicarboxylic acid (a3) (unit:mol)).

USE - The produced energy ray curable resin is useful for a resist composition.

ADVANTAGE - The energy ray curable resin can be produced without employing a halogen type catalyst (or with the reduced amount of the halogen type catalyst) and thereby the amount of the halogen ions remaining in the resulting coat is reduced. The resulting energy ray curable resin composition shows good basic properties as resist use composition, such as low tackiness, good developability, high stability, high sensitivity, high resolution and good mechanical properties.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: PROCESS PRODUCE ENERGY RAY CURE RESIN USEFUL RESIST AMOUNT HALOGEN TYPE CATALYST REDUCE

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] To energy lines, such as the manufacture approach of the energy-line hardening mold resin group excellent in hardened material nature and ultraviolet rays, and an electron ray, this invention is high sensitivity, and development with an alkali water solution is possible for it, it is excellent in the thermal resistance of the hardening film, a degree of hardness, ductility, and an electrical property, and relates to the optimal energy-line hardening mold resin constituent for the application of permanent protective masks, such as a solder resist for printed wiring substrates, etc.

[0002]

[Description of the Prior Art] Since it is also called partial saturation epoxy ester resin or vinyl ester resin and thermal resistance, chemical resistance, adhesion, and a mechanical characteristic are excellent compared with other acrylic oligomer, epoxy acrylate resin is widely used as an object for the solder resists of various coating ingredients, a structural material, and a wiring substrate etc.

[0003] Especially about the solder resist, much of minute-ization of a pattern is expected along with the increment in substrate amount of information, and the solder resist by the photo-engraving process is used. Although there is a method of developing unexposed part ink with a solvent or dilute-alkali liquid as this technique, it is the pollution problem of cost or a solvent and dilute-alkali liquid development is in use.

[0004] The so-called acid pendant mold epoxy acrylate resin which made the acid anhydride react to the hydroxyl group of epoxy acrylate resin, and made the carboxyl group pendant-ize as these dilute-alkali development mold solder resists is a principal component.

[0005] For example, the constituent which made the subject the compound to which the hydroxyl group and acid anhydride of bisphenol mold epoxy (** fluorene) acrylate were made to react is indicated by JP,5-339356,A. Since the ratio of the mol number which is the mol number and acrylic acid (meta) of an epoxy group of . epoxy resin is the equivalent, it makes the 2nd class hydroxyl group and acid anhydride of epoxy acrylate resin which were obtained react, in case this epoxy acrylate is compounded. Generally, the reactivity of the 2nd class hydroxyl group is scarce, and direct esterification with the carboxyl group and the 2nd class hydroxyl group which are generated from the ring opening reaction of an acid anhydride needs to use the high halogen system ionicity strong base catalyst of catalytic activity etc., in order to perform said reaction, since it is difficult. Since these catalysts remain in a system, the resist energy-line hardening mold resin constituent which combined the epoxy resin etc. with the obtained acid pendant mold epoxy acrylate resin as a curing agent has the technical problem that pot life is very short and there is a fall of physical properties, such as an electrical property by mixing of the halogen system ionicity matter.

[0006]

[Problem(s) to be Solved by the Invention] The technical problem of this invention can be manufactured in view of the above-mentioned technical problem also under conditions [****], such as reduction of the amount used, such as a halogen system catalyst, and use of a non-halogen system catalyst. It is in

offering the manufacture approach of the energy-line hardening mold resin which is excellent in the engine performance fundamental to reduction of the halogen system ionicity matter which remains in a paint film as a constituent for resists useful, and may improve physical properties, such as toughness, sharply, and an energy-line hardening mold resin constituent.

[0007]

[Means for Solving the Problem] As a result of inquiring wholeheartedly, this invention persons 2 functionality epoxy resin (a1), (Meta) If the dicarboxylic acid (a3) containing the dicarboxylic acid which has the monocarboxylic acid (a2) and (meta) the acryloyl radical which have an acryloyl radical is used at the following type (1) and a rate in which each (2) is satisfied Since a hydroxyl-group content denaturation epoxy acrylate compound can be fundamentally manufactured by the reaction of an epoxy group and a carboxylic acid, reduction of strong base catalysts, such as a halogen system catalyst, etc. and modification for a non-halogen system catalyst are possible. In order that it being able to manufacture with a sufficient precision and dicarboxylic acid (a3) may play a role of a chain expanding agent of epoxy acrylate, It is possible to use a comparatively low-molecular epoxy resin as a start raw material, And the energy-line hardening mold resin (I) of the structure which carried out the pendant of the carboxylic acid into the molecule which the hydroxyl group and acid anhydride in the obtained epoxy acrylate compound are made to react, and is obtained It found out that the energy-line hardening mold resin constituent made to contain with an epoxy compound (II) was excellent in the engine performance fundamental as an energy-line hardenability resin constituent for resists, and might improve physical properties, such as toughness, sharply etc.

$$0.9na1 < na2 + na3 < 1.1na1 \quad (1)$$

$$0.2 < na2/na3 < 4.0 \quad (2)$$

[-- the inside of a formula and na1 -- the mol of all the epoxy groups in an epoxy resin (a1) -- a number and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

[0008] Although the demineralization acid reaction of various phenolic compounds and epichlorohydrin performs manufacture of a common epoxy resin, in manufacture of the epoxy resin of a macromolecule, it is difficult to manufacture the epoxy resin of a high grade at the ring closure and washing process of such epichlorohydrin reaction time. Therefore, since hydrolysis nature chlorine, the hydroxyl-group component which was not able to carry out a ring closure will be contained in resin and the halogen system ionicity matter will be contained on the resist hardening film, a problem arises in physical properties. The direction of a low-molecular epoxy resin is a high grade, and the epoxy resin start raw material used by such reason for resists has it. [desirable] However, the epoxy acrylate compounded from the low-molecular epoxy resin produces a tuck (adhesiveness) after solvent desiccation, and use is difficult. The tuck nature after solvent desiccation affects the ball up, the dirt, or the workability of the negative film used at the time of exposure of ultraviolet rays etc., and is the important engine performance, and it is desirable that he is a tuck free-lancer fundamentally.

[0009] In this invention, it becomes possible to conquer this trouble by going via the chain expanding reaction by dicarboxylic acid (a3) also by use of such a low-molecular epoxy resin. Moreover, in order that the structure of a molecule may grow up to be a linear as compared with the epoxy acrylate which used epoxy common novolak type as the start raw material, the physical properties after hardening are also good and big effectiveness is shown especially in respect of toughness.

[0010] Moreover, since this chain expanding reaction is performed by the reaction of the carboxyl group of dicarboxylic acid (a3), and an epoxy group, manufacturing under conditions [****] is possible. Without control of side reaction, the field of repeatability, and the catalyst of still stronger activity using it, since it can manufacture, this has the merit further.

[0011] Moreover, the dicarboxylic acid (a3) used as this chain expanding agent shows effectiveness to the improvement in the sensibility at the time of exposure, definition, etc. by having the structure containing an acryloyl (meta) radical. By using together the dicarboxylic acid (a31) which contains 1-6 acryloyl radicals especially (meta), and the dicarboxylic acid (a32) which does not contain an acryloyl radical, it is possible to balance sensibility, the mechanical physical properties of a hardened material,

and development nature, and it is still more effective.

[0012] Namely, this invention uses as an indispensable component the dicarboxylic acid (a3) containing the dicarboxylic acid which has the monocarboxylic acid (a2) and (meta) the acryloyl radical which have 2 functionality epoxy resin (a1) and an acryloyl (meta) radical. It uses at the following type (1) and a rate in which each (2) is satisfied, and the manufacture approach of the energy-line hardening mold resin characterized by making the hydroxyl-group content denaturation epoxy acrylate compound (A) which was made to react under existence of a catalyst and was obtained, and an acid anhydride (B) react is offered.

$$0.9na1 < na2 + na3 < 1.1na1 \quad (1)$$

$$0.2 < na2/na3 < 4.0 \quad (2)$$

[-- the inside of a formula and na1 -- the mol of all the epoxy groups in an epoxy resin (a1) -- a number and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

[0013] Moreover, the monocarboxylic acid with which this invention has 2 functionality epoxy resin (a1) and an acryloyl (meta) radical (a2), The dicarboxylic acid (a3) containing the dicarboxylic acid which has an acryloyl radical is used as an indispensable component. (Meta) The hydroxyl-group content denaturation epoxy acrylate compound which used at the following formula (1) and a rate in which each (2) is satisfied, was made to react under existence of a catalyst, and was obtained (A), And the energy-line hardening mold resin (I) which the acid anhydride (B) was made to react and was obtained, and the energy-line hardening mold resin constituent characterized by containing an epoxy compound (II) are offered.

$$0.9na1 < na2 + na3 < 1.1na1 \quad (1)$$

$$0.2 < na2/na3 < 4.0 \quad (2)$$

[-- the inside of a formula and na1 -- the mol of all the epoxy groups in an epoxy resin (a1) -- a number and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

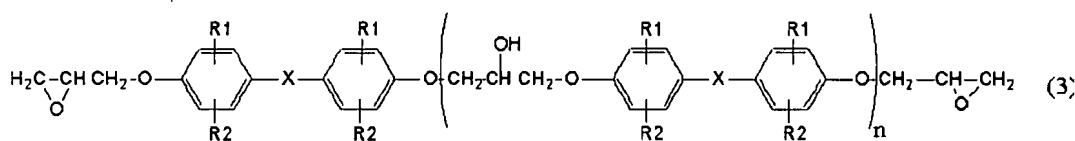
[0014]

[Embodiment of the Invention] This invention is explained below at a detail. 2 functionality epoxy resin (a1) used by this invention It is what has two or more epoxy groups in intramolecular. As the example of representation The bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, Bisphenol mold epoxy resins, such as a bisphenol smooth S form epoxy resin; The bisphenol A novolak mold epoxy resin, A bisphenol F novolak mold epoxy resin, a bisphenol S novolak mold epoxy resin, A cresol novolak mold epoxy resin, a phenol novolak mold epoxy resin, Epoxidation of the naphthols which have a naphthalene frame, and these novolak objects is carried out. novolak mold epoxy resin [, such as a xylenol novolak mold epoxy resin,]; -- epoxy resin [of dicyclopentadiene denaturation]; -- glycidyl ester mold resin [of epoxy resin; polyvalent carboxylic acid]; of the naphthalene frame obtained -- a line -- an aliphatic series epoxy resin; hydrogenation bisphenol A mold epoxy resin -- cycloaliphatic-epoxy-resin [, such as a hydrogenation bisphenol female mold epoxy resin,]; -- triglycidyl isocyanurate and its derivative; -- with glycidyl group content partial saturation monomers, such as poly glycidyl (meta) acrylate and glycidyl (meta) acrylate It can do, and by the military requirement for which it asks, the time of mentioning a copolymer with other partial saturation monomers etc. may use these epoxy resins independently, and may mix and use two or more kinds.

[0015] As said 2 functionality epoxy resin (a1), the epoxy resins and these hydrogenation objects of the bisphenol mold in which that whose weight per epoxy equivalent is the range of 140-250g g (g/eq)/Eq is more nearly especially desirable in respect of the repeatability at the time of composition, development nature, and hardened material nature, and is shown by the following general formula are more desirable especially.

General formula (3)

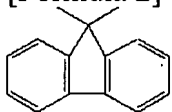
[Formula 1]



(A hydrogen atom or the alkyl group of carbon numbers 1-5 is shown by the inside R1 and R2 of a formula, X shows single bond or -CO-, -SO2-, -C(CF3)2-, -Si(CH3)2-, -CH2-, -C(CH3)2-, -O-, or the following structure expression (4), and n is the integer of 0-10.)

Structure expression (4)

[Formula 2]



(4)

[0016] As a still more desirable epoxy resin, the bisphenol A mold epoxy resin, bisphenol female mold epoxy resins, and these hydrogenation objects are mentioned, and especially the thing whose weight per epoxy equivalent of these epoxy resins is the range of 170-250g g (g/eq)/Eq especially is desirable.

[0017] As monocarboxylic acid (a2) which has the acryloyl radical used by this invention (meta), an acrylic acid and/or a methacrylic acid are desirable, or these dimer acid and trimer acids can be used.

The compound obtained by the reaction of the compound and acid anhydride which, furthermore (meta), have an acryloyl radical and a hydroxyl group can be used. These monocarboxylic acid can be used by one sort or more than it.

[0018] As a compound which has the acryloyl radical used as a raw material of said monocarboxylic acid (a2) (meta), and a hydroxyl group For example, hydroxyethyl (meta) acrylate, HIDOROKI propyl (meta) acrylate, Hydroxyalkyl (meta) acrylate, such as hydroxy butyl (meta) acrylate and hydroxy cyclohexyl (meta) acrylate; Trimethylol propane monochrome (meta) acrylate, Trimethylol propane diacrylate, pentaerythritol monochrome (meta) acrylate, Pentaerythritol di(metha)acrylate, pen TAERISURITORUTORI (meta) acrylate, Pentaerythritol di(metha)acrylate, JIPENTAERISURITORUTORI (meta) acrylate, Dipentaerythritol tetrapod (meta) acrylate, It esterifies with polyols, such as dipentaerythritol PENTA (meta) acrylate, and an acrylic acid (meta). The compound which has a hydroxyl group in the molecule with the compound obtained; The epoxy (meta) acrylate which the epoxy compound and acrylic acid (meta) which have an epoxy group are made to react to intramolecular, and is obtained, The thing which made annular lactone, such as epsilon caprolactone, react to the compound which has the above-mentioned hydroxyl group and an acrylate (meta) radical, The compound which cyclic ether compounds, such as ethyleneoxide, propylene oxide, butylene oxide, and a tetrahydrofuran, are made to react to the compound which has the above-mentioned hydroxyl group and an acrylate (meta) radical, and is obtained can be mentioned.

[0019] Moreover, as an acid anhydride used as a raw material of said monocarboxylic acid (a2), a maleic anhydride, phthalic anhydride, a succinic anhydride, a dodecenyl succinic anhydride, an anhydrous tetrahydrophthalic acid, 4-methyl-tetrahydro phthalic anhydride, 4-methyl-hexahydro phthalic anhydride, anhydrous hexahydrophthalic acid, etc. can be mentioned, for example.

[0020] The dicarboxylic acid (a3) containing the dicarboxylic acid which has the acryloyl radical used by this invention (meta) may not contain the compound which has an acryloyl (meta) radical and two carboxyl groups as an indispensable dicarboxylic acid component, and may contain the dicarboxylic acid which does not have as occasion demands further, other dicarboxylic acid, for example, (meta), acryloyl radical. It is desirable that it is dicarboxylic acid containing the dicarboxylic acid (a31) which has 1-6 acryloyl radicals especially as said dicarboxylic acid (a3) as dicarboxylic acid (meta) which has an acryloyl (meta) radical. Furthermore, it is dicarboxylic acid which the compound which has an acryloyl (meta) radical and a hydroxyl group, and a tricarboxylic acid anhydride and/or a tetracarboxylic acid anhydride are made to react as this dicarboxylic acid (a31), and is obtained, and the dicarboxylic acid (a31') which has 1-6 acryloyl (meta) radicals is desirable, and especially the dicarboxylic acid that

has 2-6 acryloyl (meta) radicals is desirable in this carboxylic acid (a31').

[0021] As a compound which has the aforementioned (meta) acryloyl radical and a hydroxyl group For example, hydroxyethyl (meta) acrylate, HIDOROKI propyl (meta) acrylate, Hydroxyalkyl (meta) acrylate, such as hydroxy butyl (meta) acrylate and hydroxy cyclohexyl (meta) acrylate; Trimethylol propane monochrome (meta) acrylate, Trimethylol propane diacrylate, pentaerythritol monochrome (meta) acrylate, Pentaerythritol di(metha)acrylate, pen TAERISURITORUTORI (meta) acrylate, Pentaerythritol di(metha)acrylate, JIPENTAERISURITORUTORI (meta) acrylate, Polyols, such as dipentaerythritol tetrapod (meta) acrylate and dipentaerythritol PENTA (meta) acrylate, The compound which has a hydroxyl group with the compound which is made to carry out the esterification reaction of the acrylic acid, and is obtained; The epoxy (meta) acrylate which the epoxy compound and acrylic acid (meta) which have an epoxy group are made to react to intramolecular, and is obtained, (Meta) The compound which annular lactone, such as epsilon-caprolactone, is made to react to the compound which has these (meta) acryloyl radical and a hydroxyl group, and is obtained, The compound which cyclic ether compounds, such as ethyleneoxide, propylene oxide, butylene oxide, and a tetrahydrofuran, are made to react to the compound which has these (meta) acryloyl radical and a hydroxyl group, and is obtained is mentioned.

[0022] Moreover, as a tricarboxylic acid anhydride, they are trimellitic anhydride and naphthalene, for example. - The anhydride of tricarboxylic acid, such as 1, 2, and 4-tricarboxylic acid anhydride, is mentioned.

[0023] As a tetracarboxylic acid anhydride, for example Furthermore, pyromellitic acid 2 anhydride, Benzophenone -3, 3', 4, and 4'-tetracarboxylic dianhydride, Diphenyl ether -3, 3', 4, and 4'-tetracarboxylic dianhydride, Benzene - 1, 2, 3, 4-tetracarboxylic dianhydride, biphenyl -3, 3', 4, and 4'-tetracarboxylic dianhydride, Biphenyl -2, 2', 3, and 3'-tetracarboxylic dianhydride, naphthalene - 2, 3, 6, 7-tetracarboxylic dianhydride, Naphthalene - 1, 2, 4, 5-tetracarboxylic dianhydride, naphthalene - 1, 4, 5, 8-tetracarboxylic dianhydride, Decahydronaphthalene - 1, 4, 5, 8-tetracarboxylic dianhydride, 4, 8-dimethyl - 1, 2, 3, 5, 6, 7-hexahydro naphthalene - 1, 2, 5, 6-tetracarboxylic dianhydride, 2, 6-dichloro naphthalene -1, 4 and 5, and 8-tetracarboxylic dianhydride 2, 7-dichloro naphthalene - 1, 4, 5, 8-tetracarboxylic dianhydride, 2, 3, 6, 7-tetrachloronaphthalene - 1, 4, 5, 8-tetracarboxylic dianhydride, Phenanthrene - 1, 3, 9, 10-tetracarboxylic dianhydride, BERIREN - 3, 4, 9, 10-tetracarboxylic dianhydride, Bis(2, 3-dicarboxy phenyl) methane 2 anhydride, bis(3, 4-dicarboxy phenyl) methane 2 anhydride, 1 and 1'-bis(2, 3-dicarboxy phenyl) ethane 2 anhydride, 1 and 1'-bis(3, 4-dicarboxy phenyl) ethane 2 anhydride, 2 and 2'-bis(2, 3-dicarboxy phenyl) propane 2 anhydride, The anhydride of the tetracarboxylic acid which has aromatic series organic radicals, such as 2, 3-bis(3, 4-dicarboxy phenyl) propane 2 anhydride, bis(3, 4-dicarboxy phenyl) sulfone 2 anhydride, and bis(3, 4-dicarboxy phenyl) ether 2 anhydride, is mentioned. These can be used [respectively independent or] by two or more sorts. Moreover, these may be mixed and used for the anhydride of tricarboxylic acid, and the anhydride of tetracarboxylic acid.

[0024] The dicarboxylic acid (a31') which has the 1-6 aforementioned (meta) acryloyl radicals can be obtained by making the hydroxyl group of the compound which has for example, an acryloyl (meta) radical and a hydroxyl group, and the acid anhydrous radical of a tricarboxylic acid anhydride and/or a tetracarboxylic acid anhydride react at the temperature of 50-140 degrees C. under a reaction with the epoxy group to which the rate of an use rate of a hydroxyl group and an acid anhydrous radical does not remain, but an acid anhydrous radical performs it henceforth at this time -- gelation and side reaction -- molecular weight distribution -- large -- 7 -- ** -- a ** -- development nature etc. -- good -- maintaining -- Moreover, in order to lose the unreacted component of the compound which has the acryloyl (meta) radical and hydroxyl group in a system and to keep good the tuck nature after solvent temporary desiccation, it is desirable to react within limits from which the mole ratio (OH / acid anhydrous radical) of a hydroxyl group and an acid anhydrous radical is set to 0.8-1.4.

[0025] (Meta) As an example of dicarboxylic acid (a31') of having 1-6 acryloyl radicals, it is the ring breakage esterification object of hydroxyethyl acrylate, half esterification object [of trimellitic anhydride] and pentaerythritol thoria chestnut rate, half esterification object [of trimellitic anhydride]

and two mols of hydroxyethyl acrylate, ring breakage esterification object [of pyromellitic acid 2 anhydride] and pentaerythritol thoria chestnut rate, and pyromellitic acid 2 anhydride, and the dicarboxylic acid which has 1-6 acryloyl (meta) radicals is mentioned.

[0026] moreover, as dicarboxylic acid (a3) containing the dicarboxylic acid which has the acryloyl radical used by this invention (meta) An acryloyl radical 1-6 (Meta) That it is dicarboxylic acid which comes to use together the dicarboxylic acid (a31) which it has, and the carboxylic acid (a32) which does not have an acryloyl (meta) radical It is desirable from the hardened material which is excellent in toughness being obtained, and excels in the balance of sensibility and toughness especially. and from the good engine performance being shown also in development nature etc. It is still more desirable that it is the range where the ratio (na31/na32) of the number of mols (na31) of all the carboxyl groups in dicarboxylic acid (a31) and the number of mols (na32) of all the carboxyl groups in dicarboxylic acid (a32) becomes 1-10. It is most desirable that it is the range used as 1-10.

[0027] As dicarboxylic acid (a32) which does not have the aforementioned (meta) acryloyl radical, a succinic acid, a fumaric acid, a phthalic acid, an itaconic acid, an adipic acid, an azelaic acid, a sebacic acid, a phthalic acid, isophthalic acid, a terephthalic acid, a tetrahydrophthalic acid, hexahydrophthalic acid, the dicarboxylic acid that a monoalcohol compound is made to react to a tricarboxylic acid anhydride and a tetracarboxylic acid anhydride which were further described above, and is obtained are mentioned, for example. The compound which has one hydroxyl group which denaturalized phenolic compounds, such as alkyl alcoholic; phenols, such as a methanol, ethanol, a butanol, and a pentanol, cresol, and alkylphenol, in alkylene oxide, such as ethyleneoxide, propylene oxide, and butylene oxide, as a monoalcohol compound here, for example is mentioned.

[0028] Moreover, although it is the range which does not spoil the effectiveness that this invention does so, as said dicarboxylic acid (a3) and little concomitant use of the acid anhydride can also be carried out as the part, usually not using together is desirable.

[0029] Under existence of a catalyst, manufacture of the hydroxyl-group content denaturation epoxy acrylate compound (A) used by this invention may make 2 functionality epoxy resin (a1) and the dicarboxylic acid (a3) which has the monocarboxylic acid (a2) and (meta) the acryloyl radical which have an acryloyl (meta) radical react to coincidence, or may perform it to serial.

[0030] The reaction of said epoxy resin (a1), and said monocarboxylic acid (a2) and dicarboxylic acid (a3) is a reaction of the epoxy group of an epoxy resin (a1), and the carboxyl group in monocarboxylic acid (a2) and dicarboxylic acid (a3), and an esterification reaction advances comparatively quantitatively on mild conditions. Since partial saturation monocarboxylic acid (a2) has one carboxylic acid, it functions as a stopper of molecule growth, and dicarboxylic acid (a3) functions as a chain expanding agent which connects a molecule.

[0031] As for this reaction, it is indispensable that the following type (1) and all of (2) satisfy an epoxy resin (a1), and monocarboxylic acid (a2) and dicarboxylic acid (a3).

$$0.9na1 < na2 + na3 < 1.1na1 \quad (1)$$

$$0.2 < na2/na3 < 4.0 \quad (2)$$

[-- the inside of a formula and na1 -- the mol of all the epoxy groups in an epoxy resin (a1) -- a number and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

[0032] the mol of all the carboxyl groups in monocarboxylic acid (a2) -- the mol of a number and all the carboxyl groups in dicarboxylic acid (a3) -- the sum of a number -- the mol of all the epoxy groups in an epoxy resin (a1) -- it is 0.9 to 1.1 times the number.

[0033] the mol of all the carboxyl groups in monocarboxylic acid (a2) -- the mol of a number and all the carboxylic acids in dicarboxylic acid (a3) -- the sum of a number -- the mol of all the epoxy groups in an epoxy resin (a1) -- in order an epoxy group remains and after reaction termination has a bad influence on stability etc., and for an acid to remain and to have a bad influence on an odor, stability, etc. when larger than 1.1 times when a number is smaller than 0.9 times, it is not desirable respectively.

[0034] Moreover, in said formula (2), the ratio (na2/na3) of the number of mols (na2) of all the carboxyl groups in monocarboxylic acid (a2) and the number of mols (na3) of all the carboxylic acids in

dicarboxylic acid (a3) is within the limits of 0.2-4.0.

[0035] Since the molecular weight of a hydroxyl-group content denaturation epoxy acrylate compound (A) becomes large too much and development nature and desiccation management width of face become short when a mole ratio (n_2/n_3) is smaller than 0.2, it is not desirable. Moreover, when a mole ratio (n_2/n_3) is larger than 4.0, molecule growth of a hydroxyl-group content denaturation epoxy acrylate compound (A) is not performed, but a problem is produced to the tuck nature after temporary desiccation of a solvent, and it is not desirable. As for a mole ratio (n_2/n_3), it is desirable that it is $0.3 < n_2/n_3 < 3$ especially in respect of development nature, desiccation management width of face, and a tuck, and it is desirable that it is especially $0.8 < n_2/n_3 < 2$.

[0036] As for reaction temperature, it is desirable to be able to carry out in 70-170 degrees C, and to carry out within the limits of 80-160 degrees C especially especially in respect of reduction of side reaction, control of molecular weight distribution, and reaction time.

[0037] Moreover, although a catalyst is used at the time of manufacture, physical properties may use stabilizers, such as polymerization inhibitor and an antioxidant, in the disadvantage range which is not *****. It is desirable to be able to use a small amount of halogen system catalyst in 10-3,000 ppm as a catalyst to all the charges of a non-halogen system catalyst or an epoxy resin (a1), monocarboxylic acid (a2), and dicarboxylic acid (a3), and to use a non-halogen system catalyst especially.

[0038] Said non-halogen system catalyst is desirable. For example, triethylamine, tris dimethylamino methyl phenol, tertiary amine system catalyst [, such as benzyl dimethylamine,]; -- tetramethyl ammonium hydroxide; -- 2-methylimidazole -- imidazole system catalyst [, such as 2-ethyl-4-methylimidazole,]; -- nitride system catalyst [, such as diaza screw cyclo undecene,]; -- a triethyl phosphine -- A tree n-propyl phosphine, tri-n-butyl phosphine, a tree m-tolyl phosphine, Phosphonium salt system catalysts, such as phosphine system catalyst; tetra--n-butyl phosphonium hydroxide, such as a tris (2, 6-methoxyphenyl) phosphine and triphenyl phosphine; various catalysts, such as metal salt system catalysts, such as naphthenic-acid chromium, can be used. Among these, the Lynn system catalysts, such as a phosphine system catalyst and a phosphonium salt system catalyst, are desirable, and especially a phosphine system catalyst is desirable especially. As amount of the non-[these] halogen system catalyst used, 10-10,000 ppm is a fitness amount to the total charge of an epoxy resin (a1), monocarboxylic acid (a2), and dicarboxylic acid (a3).

[0039] Moreover, as a halogen system catalyst, phosphonium salt, such as quarternary-ammonium-salt; tetra--n-butyl phosphonium star's pictures, such as inorganic-catalyst; trimethyl benzylammonium chloride, such as a sodium hydroxide and hydroxylation lithium, and tetramethyl ammoniumchloride, and an ethyltriphenylphosphonium star's picture, is mentioned, for example.

[0040] As polymerization inhibitor, hydroquinone, methyl hydroquinone, trimethyl hydroquinone, tertiarybutyl hydroquinone, 2-6-di-tertiary-butyl-4-methoxyphenol, copper salt, phenothiazin, etc. are mentioned, for example.

[0041] As an anti-oxidant, phosphorous acid, phosphite, and phosphorous acid diester are mentioned, for example.

[0042] In order that the molecular weight of the hydroxyl-group content denaturation epoxy acrylate compound (A) used by this invention may make good the tuck nature and the machine physical properties after solvent desiccation and may make development nature fitness, it is desirable that it is within the limits of 2,000-40,000 in the weight average molecular weight of within the limits of 1,000-20,000 and polystyrene conversion at the number average molecular weight of polystyrene conversion.

[0043] In this way, the energy-line hardening mold resin (I) which the hydroxyl-group content denaturation epoxy acrylate compound (A) and acid anhydride (B) which were obtained are made to react, and is made into the purpose can be manufactured.

(0044) As an acid anhydride (B) used here, a maleic anhydride, phthalic anhydride, a succinic anhydride, a dodecenyl succinic anhydride, an anhydrous tetrahydrophthalic acid, 4-methyl-tetrahydro phthalic anhydride, 4-methyl-hexahydro phthalic anhydride, anhydrous hexahydrophthalic acid, trimellitic anhydride, an anhydrous methyl NAJIKKU acid, itaconic acid anhydride, pyromellitic dianhydride, a benzophenone tetracarboxylic acid anhydride, etc. are mentioned, for example.

[0045] As the manufacture approach of energy-line hardening mold resin (I), the 130 degrees C of the 0.15 mols or more of the approaches of making react at 50-110 degrees C preferably, and carrying out pendant esterification are preferably mentioned from ordinary temperature in a 0.3-0.95-mol acid anhydride (B) to one mol of hydroxyl groups in a hydroxyl-group content denaturation epoxy acrylate compound (A), for example. The hydroxyl group in a hydroxyl-group content denaturation epoxy acrylate compound (A) serves as a hydroxyl group contained in an epoxy resin (a1), and the number of mols of the sum of the number of mols to which all the carboxylic acids in monocarboxylic acid (a2) and dicarboxylic acid (a3) reacted here. Moreover, as the acid number of a hydroxyl-group content denaturation epoxy acrylate compound (A), it is desirable to become the range of 30 - 120 mgKOH/g, and it is desirable to become 40 - 100 mgKOH/g especially especially in respect of development nature or hardened material nature.

[0046] The reaction terminal point of the hydroxyl group in a hydroxyl-group content denaturation epoxy acrylate compound (A) and the acid anhydrous radical in an acid anhydride (B) can be checked because the acid-anhydride peak of infrared spectroscopy spectrum 1770cm-1 and 1850cm-1 disappears.

[0047] In order that the molecular weight of the energy-line hardening mold resin (I) obtained by this manufacture approach may make good the tuck nature and the machine physical properties after solvent desiccation and may make development nature fitness, it is desirable that it is within the limits of 2,500-40,000 in the weight average molecular weight of within the limits of 1,500-20,000 and polystyrene conversion at the number average molecular weight of polystyrene conversion.

[0048] Furthermore, said energy-line hardening mold resin (I) can be used as the energy-line hardening mold resin constituent suitable as an object for resists machine physical properties, whose heat-resistant physical properties, etc. improved by making the carboxyl group after the pattern creation by after ultraviolet-rays exposure and development, and in energy-line hardening mold resin (I), and the epoxy compound (II) which can react exist in a constituent.

[0049] Although not restricted especially, the epoxy compound which has two or more epoxy groups is [that an epoxy compound (II) should just be a compound which has an epoxy group] desirable. As the typical example The bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, A bisphenol smooth S form epoxy resin, a phenol novolak mold epoxy resin, A cresol novolak mold epoxy resin, the glycidyl ester mold epoxy resin of polyvalent carboxylic acid, Cycloaliphatic epoxy resin, such as a hydrogenation bisphenol A mold epoxy resin and a hydrogenation bisphenol female mold epoxy resin, Triglycidyl isocyanurate resin, a dicyclopentadiene conversion epoxy resin, Epoxy resins, such as an epoxy resin of a naphthalene frame, an epoxy resin guided from the xylenol, a phenol aralkyl epoxy resin, and a naphthalene aralkyl epoxy resin, other ZAIROKKU mold epoxy resins, can be mentioned.

[0050] Said epoxy compound (II) may be independent, or may use two or more sorts together. Although there is especially no limit in the amount used, the range which serves as the 5 - 300 weight section to the solid content 100 weight section of an energy-line hardening mold resin constituent is desirable, and especially the range that serves as the 10 - 100 weight section especially is desirable.

[0051] Furthermore, an epoxy hardening accelerator can be added in the range which does not spoil the effectiveness of this invention for promotion of a reaction.

[0052] As an epoxy hardening accelerator, various kinds of epoxy hardening accelerators, such as amine compounds, imidazole compounds, dialkylurea, carboxylic acids, phenols, and methylol radical content compounds, can be mentioned, for example. These hardening accelerators can make many physical properties of a resist coat improve through the reaction of an epoxy compound and the carboxyl group in energy-line hardening mold resin, and the reaction of epoxy compounds while promoting the polymerization of an energy-line hardening component by carrying out afterbaking of the paint film.

[0053] In case it hardens by UV irradiation, a photopolymerization initiator and a photosensitizer can be used for the energy-line hardening mold resin constituent of this invention.

[0054] Various kinds of photopolymerization initiators can be used as a photopolymerization initiator. For example, 4-dimethylamino benzoic acid, 4-dimethylamino benzoate, An alkoxy acetophenone, a benzophenone, and a benzophenone derivative, Benzoylbenzoic acid alkyl, a bis(4-dialkyl aminophenyl)

ketone, Benzyl and a benzyl derivative, a benzoin, and a benzoin derivative, Benzoin alkyl ether, 2-hydroxy-2-methylpropiohenone, 1-hydroxy cyclohexyl phenyl ketone, 2 and 4, 6-trimethyl benzoyl JIFENOIRU phosphine oxide, The 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino propane -1, 2-benzyl-2-dimethylamino -1 -(4-morpholino phenyl)- Butanone -1, an acetophenone, A 2 and 2-dimethoxy-2-phenyl acetophenone, 2, and 2-diethoxy-2-phenyl acetophenone, Acetophenones, such as 1 and 1-dichloro acetophenone, 2-methyl anthraquinone, 2-ethyl anthraquinone, 2-tertiarybutyl anthraquinone, To 1-chloro anthraquinone, 2-aluminum anthraquinone, etc., anthraquinone 2, 4-dimethyl thioxan ton, 2, 4-diethylthio xanthone, Ketals, such as thioxan tons, such as 2-chloro thioxan ton, 2, and - diisopropyl thioxan ton, acetophenone dimethyl ketal, and benzyl dimethyl ketal, and xanthonnes are mentioned.

[0055] The amount of the photopolymerization initiator used is usually range which serves as 0.2 - 30 weight section to the solid content 100 weight section of an energy-line hardening mold resin constituent, and is range which serves as 2 - 20 weight section preferably. This photopolymerization initiator can also be used combining a kind or two sorts or more.

[0056] In the energy-line hardening type fat constituent of this invention, other photopolymerization nature compounds can also be used together for the purpose, such as reforming of the physical properties of the hardening film, amelioration of hardenability, and reforming of paint fitness. Although especially a limit does not have the photopolymerization nature compound used and various kinds of photopolymerization nature vinyl monomers and oligomer can be used As a typical example, beta-hydroxyethyl (meta) acrylate, beta-hydroxypropyl (meta) acrylate, glycidyl (meta) acrylate, beta-hydroxyethyl (meta) acryloyl phosphate, dimethylaminoethyl (meta) acrylate, Diethylaminoethyl (meta) acrylate, ethylene glycol di(metha)acrylate, Diethylene GURIKORUJI (meta) acrylate, triethylene glycol di(metha)acrylate, Pori ethylene glycol di(metha)acrylate, propyleneglycol di(meth) acrylate, Zypro pyrene GURIKORUJI (meta) acrylate, Tori propyleneglycol di(meth) acrylate, Pori propyleneglycol di(meth) acrylate, TORIMECHI roll pro pansy (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, Pentaerythritol tetrapod (meta) acrylate, dipentaerythritol tetrapod (meta) acrylate, Dipentaerythritol PENTA (meta) acrylate, dipentaerythritol hexa (meta) acrylate, The monomers which have acryloyl (meta) radicals, such as tris (2-(meta) acryloyloxyethyl) isocyanurate; Monod of polybasic acid and hydroxyalkyl (meta) acrylate, G, a tree, or the polyester (meta) acrylate compound beyond it, The oligomer which has acryloyl (meta) radicals, such as bisphenol mold epoxy (meta) acrylate, novolak mold epoxy (meta) acrylate, and urethane acrylate, can be mentioned.

[0057] In this invention, an organic solvent can be used for improvement in stirring effectiveness when compounding resin, reduction of viscosity, and amelioration of handling nature or application fitness.

[0058] As an organic solvent, ethers solvents and acetic ester, such as carbitol; ethyl acetate, such as cellosolve; carbitols, such as aromatic hydrocarbon; cellosolves, such as ketones; toluene, such as a methyl ethyl ketone and a cyclohexanone, and a xylene, and butyl cellosolve, and butyl carbitol, butyl acetate, a cellosolve acetate, butyl-cellosolve acetate, carbitol acetate, ethyl carbitol acetate, and butyl carbitol acetate, etc. are mentioned, for example.

[0059] The above photopolymerization nature compounds and/or organic solvents are independent, or can be used as two or more sorts of mixture. The range where the amount used is desirable has the desirable range which serves as the 5 - 300 weight section to the solid content 100 weight section of an energy-line hardening mold resin constituent, and it is the range which serves as the 10 - 200 weight section more preferably.

[0060] Various kinds of pigments for coloring, such as various kinds of bulking agents, such as a barium sulfate, silicon oxide, talc, clay, and a calcium carbonate, a copper phthalocyanine blue, Phthalocyanine Green, titanium oxide, and carbon black, a defoaming agent, an adhesion grant agent, a leveling agent, a slipping agent, etc. may be further added to the energy-line hardening mold resin constituent of this invention if needed.

[0061] A coat can be made to form by the energy-line hardening mold resin constituent of this invention being suitable as an energy-line hardening mold resin constituent for resists, and applying to various

base materials. The target coat can be made to form by there being a printed-circuit board etc. and applying this constituent on this as a base material, on the whole surface by screen printing, the roll coater method, the curtain coating-machine method, the spray coater, spin coater **, etc., for example, irradiating an energy line, melting a part for an unexposed part away in a dilute-alkali water solution after hardening a need part, and adding the postcure by heat further. Moreover, when it contains a solvent etc., solvent desiccation may be performed before the exposure of an energy line.

[0062] The energy line as used in the field of this invention names generically ionizing radiation, light, etc. like an electron ray, alpha rays, a gamma ray, an X-ray, a neutron beam, and ultraviolet rays.

[0063] As the exposure light source of an energy line, when using ultraviolet rays, a low-pressure mercury lamp, a medium-voltage mercury lamp, a high-pressure mercury lamp, a xenon lamp, a metal halide lamp, etc. can use a laser beam etc. as an energy line for hardening suitably.

[0064]

[Example] Next, although an example and an application explain this invention much more concretely, unless the section and % have a notice especially in below, they shall be weight criteria altogether.

[0065] The trimellitic anhydride 153.6 section and the hydroxyethyl acrylate 92.8 section were taught to the flask equipped with example 1 thermometer, the stirrer, and the reflux condenser, and the half esterification reaction (ring breakage esterification with a hydroxyl group and an acid anhydride) was performed at 100 degrees C for 5 hours. At this time, the acid number of a system was 182 mgKOH/g. Furthermore, the esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 144 section and the triphenyl phosphine 2 section, and blowing air, after having put in the propylene-glycol-monomethyl-ether acetate 200 section into this, adding the isophthalic acid 33.2 section and the bisphenol A mold epoxy resin (weight per epoxy equivalent 188; Epiclon 850 by Dainippon Ink & Chemicals, Inc.) 752 section and adding the hydroquinone 1 section as polymerization inhibitor. At this time, the acid number of a system was 0.3 mgKOH/g and weight per epoxy equivalent was 41,000 g/eq. Then, added the propylene-glycol-monomethyl-ether acetate 466.3 section and the tetrahydro phthalic anhydride 379 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (X1) was obtained. The acid number of this resin solution was 63.4 mgKOH/g (acid-number 90.2 mgKOH/g of resin solid content).

[0066] The trimellitic anhydride 76.8 section and the pentaerythritol thoria chestnut rate (hydroxyl value = 119.9 mgKOH/g) 187.2 section were taught to the same experimental device as example 2 example 1, and the half esterification reaction (ring breakage esterification with a hydroxyl group and an acid anhydride) was performed at 100 degrees C for 5 hours. At this time, the acid number of a system was 85 mgKOH/g. The esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 172.8 section and the triphenyl phosphine 2 section, and blowing air, after having put in the ethyl carbitol acetate 200 section into this furthermore, adding the isophthalic acid 33.2 section, the terephthalic-acid 33.2 section, and the bisphenol A mold epoxy resin (weight per epoxy equivalent 188; Epiclon 850 by Dainippon Ink & Chemicals, Inc.) 752 section and adding the hydroquinone 1 section as polymerization inhibitor. At this time, the acid number of a system was 0.1 mgKOH/g and weight per epoxy equivalent was 35,000 g/eq. Then, added the ethyl carbitol acetate 511.4 section and the tetrahydro phthalic anhydride 404.8 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (X2) was obtained. The acid number of this resin solution was 63.0 mgKOH/g (acid-number 90.0 mgKOH/g of resin solid content).

[0067] The trimellitic anhydride 153.6 section and the pentaerythritol thoria chestnut rate (hydroxyl value 119.9 mgKOH/g) 374.4 section were taught to the same experimental device as example 3 example 1, and the half esterification reaction (ring breakage esterification with a hydroxyl group and an acid anhydride) was performed at 100 degrees C for 5 hours. At this time, the acid number of a system was 85 mgKOH/g. The esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 172.8 section and the triphenyl phosphine 2 section, and blowing air, after having put in the ethyl carbitol acetate 200 section into this, adding the bisphenol female mold epoxy resin (weight per epoxy equivalent 171; Epiclon 830 by Dainippon Ink & Chemicals, Inc.) 684 section further and adding the hydroquinone 1 section as polymerization inhibitor. At this time, the acid number of a

system was 0.1 mgKOH/g and weight per epoxy equivalent was 29,000 g/eq. Then, added the ethyl carbitol acetate 584.9 section and the tetrahydro phthalic anhydride 446.6 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (X3) was obtained. The acid number of this resin solution was 63.0 mgKOH/g (acid-number 90.0 mgKOH/g of resin solid content).

[0068] The ethyl carbitol acetate 200 section, the pyromellitic dianhydride 87.2 section, and the hydroxyethyl acrylate 92.8 section were taught to the same experimental device as example 4 example 1, and the half esterification reaction (ring breakage esterification with a hydroxyl group and an acid anhydride) was performed at 100 degrees C for 5 hours. At this time, the acid number of a system was 118.1 mgKOH/g (the acid number of resin solid content is 249.3 mgKOH/g). In this, the isophthalic acid 99.6 section and the bisphenol female mold epoxy resin (weight per epoxy equivalent 171; Epiclon 830 by Dainippon Ink & Chemicals, Inc.) 478.8 section, 3, 3', 5, and 5'-tetramethyl - The tetramethyl biphenyl mold epoxy resin (weight per epoxy equivalent 185; Epicoat YX4000 by oil-ized shell chemistry company) 222 section which comes to carry out epoxidation of the 4 and 4'-biphenyl diol in epichlorohydrin is added. The esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 144 section and the triphenyl phosphine 2 section, and blowing air, after adding the hydroquinone 1 section as polymerization inhibitor. At this time, the acid number of a system was 0.1 mgKOH/g and weight per epoxy equivalent was 19,000 g/eq. Then, added the ethyl carbitol acetate 367.9 section and the succinic-anhydride 200.8 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (X4) was obtained. The acid number of this resin solution was 59.5 mgKOH/g (acid-number 85.0 mgKOH/g of resin solid content).

[0069] The 153.6 sections and the pentaerythritol thoria chestnut rate (hydroxyl value 119.9 mgKOH/g) 374.4 section were taught to the same experimental device as example 5 example 1 for trimellitic anhydride, and the half esterification reaction (ring breakage esterification with a hydroxyl group and an acid anhydride) was performed at 100 degrees C for 5 hours. At this time, the acid number of a system was 85 mgKOH/g. The esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 144 section and the triphenyl phosphine 2 section, and blowing air, after having put in the ethyl carbitol acetate 387 section and the cyclohexane dicarboxylic acid 35 section into this, adding the hydrogenation bisphenol A mold epoxy resin (weight per epoxy equivalent 210; Epiclon EXA[by Dainippon Ink & Chemicals, Inc.]- 7015) 840 section further and adding the hydroquinone 1 section as polymerization inhibitor. At this time, the acid number of a system was 0.9 mgKOH/g and weight per epoxy equivalent was 22,000 g/eq. Then, added the ethyl carbitol acetate 486 section and the tetrahydro phthalic anhydride 490 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (X5) was obtained. The acid number at the time of this resin solution was 62.0 mgKOH/g (acid-number 88.0 mgKOH/g of resin solid content).

[0070] The esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 144 section and the triphenyl phosphine 2 section, and blowing air, after teaching the bisphenol A mold epoxy resin (weight per epoxy equivalent 188; Epiclon 850 by Dainippon Ink & Chemicals, Inc.) 376 section to the flask equipped with example of comparison 1 thermometer, the stirrer, and the reflux condenser and adding the hydroquinone 0.5 section to it as polymerization inhibitor. At this time, the acid number of a system was 0.5 mgKOH/g and weight per epoxy equivalent was 38,600 g/eq. Then, added the ethyl carbitol acetate 229.2 section and the tetrahydro phthalic anhydride 167.7 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (RX1) was obtained. The acid number of this resin solution was 67.2 mgKOH/g (acid-number 89.5 mgKOH/g of resin solid content).

[0071] The esterification reaction was performed at 120 degrees C for 12 hours, having added the acrylic-acid 144 section and the triphenyl phosphine 5 section, and blowing air, after having put the ethyl carbitol acetate 356 section into the flask equipped with example of comparison 2 thermometer, the stirrer, and the reflux condenser, dissolving the bisphenol A mold epoxy resin (weight per epoxy equivalent 640; Epiclon 2055 by Dainippon Ink & Chemicals, Inc.) 1280 section in it and adding the hydroquinone 1.3 section to it as polymerization inhibitor. At this time, the acid number of a system was

0.5 mgKOH/g and weight per epoxy equivalent was 51,100 g/eq. Then, added the ethyl carbitol acetate 423.2 section and the tetrahydro phthalic anhydride 394.1 section, it was made to react at 100 degrees C for 5 hours, and the energy-line hardening mold resin solution (RX2) was obtained. The acid number of this resin solution is [0072] which was 56.3 mgKOH/g (acid-number 80.5 mgKOH/g of resin solid content). Although reacted to the flask equipped with example of comparison 3 thermometer, the stirrer, and the reflux condenser by carrying out a temperature up to 120 degrees C, having added the acrylic-acid 288 section and the triphenyl phosphine 5 section, and blowing air, after having put in the ethyl carbitol acetate 356 section, dissolving the bisphenol A mold epoxy resin (weight per epoxy equivalent 640; Epilcon 2055 by Dainippon Ink & Chemicals, Inc.) 1280 section and adding the hydroquinone 1 section as polymerization inhibitor, it gelled in about 6 hours.

[0073] The esterification reaction was performed at 120 degrees C for 10 hours, having added the acrylic-acid 72 section and the triethyl benzyl ammonium chloride 0.45 section, and blowing air, after dissolving the bisphenol A mold epoxy resin (weight per epoxy equivalent 188; Epilcon 850 by Dainippon Ink & Chemicals, Inc.) 188 section in the flask equipped with example of comparison 4 thermometer, the stirrer, and the reflux condenser and adding the 2 and 6-diisobutyl phenol 0.1 section to it as polymerization inhibitor. At this time, the acid number of a system was 0.5 mgKOH/g and weight per epoxy equivalent was 23,200 g/eq. then, the ethyl carbitol acetate 203.8 section, the tetrahydro phthalic anhydride 38 section, the benzophenone tetracarboxylic dianhydride 80.5 section, and bromination -- added the tetraethyl AMMU nium 1 section, it was made to react at 115 degrees C for 5 hours, and the energy-line hardening mold resin solution (RX4) was obtained. The acid number of this resin solution was 55.9 mgKOH/g (acid-number 86 mgKOH/g of resin solid content).

[0074] The characteristics value of the resin obtained by the example and the example of a comparison is shown in the 1st table and the 2nd table.

[0075]

[Table 1]

第1表

項 目		実施例				
		1	2	3	4	5
樹脂溶液の名称		X 1	X 2	X 3	X 4	X 5
(a1)	B P A 1	4.0	4.0	—	—	—
	B P F 1	—	—	4.0	2.8	—
	T M B P	—	—	—	1.2	—
	H 1 2 B P A	—	—	—	—	4.0
(a2)	A A	2.0	2.4	2.4	2.0	2.0
(a3)	(a31)	TM-HE	1.6	0.8	—	—
		TM-PE	—	0.4	1.6	1.6
		PM-HE	—	—	0.8	—
	(a32)	I P A	0.4	0.4	—	1.2
		T P A	—	0.4	—	—
		CHDA	—	—	—	0.4
(B)	T H P A	2.49	2.66	2.94	—	3.22
	S A N	—	—	—	2.00	—
モ ル 比	$(n_{a2} + n_{a3}) / n_{a1}$	1.0	1.0	1.0	1.0	1.0
	n_{a2} / n_{a3}	1.0	1.5	1.5	1.0	1.0
	n_{a31} / n_{a32}	4.0	1.0	—	0.67	4.0
酸価 (mg KOH / g)		90.2	90.0	90.0	85.0	88.0
数平均分子量		1860	1730	1490	1490	1720
重量平均分子量		6850	6640	8950	6210	10600

[0076]

[Table 2]

第2表

項 目		比較例			
		1	2	3	4
樹脂溶液の名称		RX1	RX2	RX3	RX4
(a1)	BPA1	2.0	—	—	1.0
	BPA2	—	2.0	2.0	—
	BPF1	—	—	—	—
	TMBP	—	—	—	—
	H12BPA	—	—	—	—
(a2)	AA	2.0	2.0	4.0	1.0
(a3)	(a31)	TM-HE	—	—	—
		TM-PE	—	—	—
		PM-HE	—	—	—
	(a32)	IPA	—	—	—
		TPA	—	—	—
		CHDA	—	—	—
(a')	THPA		—	—	0.25
	BPDA _n		—	—	0.25
(B)	THPA		1.103	2.593	0.25
	SAN		—	—	—
モ ル 比	$(n_{a2} + n_{a3}) / n_{a1}$		1.0	1.0	2.0
	n_{a2} / n_{a3}		—	—	—
	n_{a31} / n_{a32}		—	—	—
酸価 (mg KOH/g)		90.5	90.2	—	86.0
数平均分子量		710	1950	—	3700
重量平均分子量		1400	4600	—	26000

[0077] Footnote [of the 1st table and the 2nd table] - (a1) : 2 functionality epoxy resin. The numeric value of front Naka is number [of an epoxy group] of preparation mols - (a2). : (meta) monocarboxylic acid which has an acryloyl radical. The numeric value of front Naka is the number of preparation mols of a carboxylic acid.

- a3 : (meta) dicarboxylic acid containing the dicarboxylic acid which has an acryloyl radical. The numeric value of front Naka is the number of preparation mols of a carboxyl group.

- a31 : (meta) dicarboxylic acid which has 1-6 acryloyl radicals. The numeric value of front Naka is the number of mols of a carboxyl group.

- a32 : (meta) dicarboxylic acid which does not have an acryloyl radical. The numeric value of front Naka is the number of mols of a carboxyl group.

- a' : polybasic acid anhydride used as a chain expanding component.

** (B) : acid anhydride. The numeric value of front Naka is the number of mols of an acid anhydride.

- BPA1 : The bisphenol A mold epoxy resin. Weight-per-epoxy-equivalent 188 g/eq-BPA2 : The bisphenol A mold epoxy resin. Weight-per-epoxy-equivalent 640 g/eq-BPF1 : Bisphenol female mold epoxy resin. Weight-per-epoxy-equivalent 171 g/eq-TMBP : Tetramethyl biphenyl diol mold epoxy

resin. Weight-per-epoxy-equivalent 185 g/eq-H12BPA : Hydrogenation bisphenol A mold epoxy resin. Weight-per-epoxy-equivalent 210 g/eq-AA : An acrylic acid and TM-HE : Trimellitic anhydride and hydroxyethyl acrylate reactant.

- TM-PE : Trimellitic anhydride and pentaerythritol thoria chestnut rate reactant.

- PM-HE : Pyromellitic dianhydride and hydroxyethyl acrylate reactant.

- IPA : Isophthalic acid, TPA : A terephthalic acid and CHDA : Cyclohexane dicarboxylic acid and THPA : Tetrahydro phthalic anhydride and SAN : A succinic anhydride and mole ratio : What showed the rate of the epoxy group in each raw material, and a carboxyl group for the operating rate of each raw material component by the mole ratio. $(na_2+na_3)/na_1$ shows the ratio of the number of sum total mols (na_2+na_3) of all the carboxyl groups in monocarboxylic acid (a_2) and dicarboxylic acid (a_3) to the na_1 mol number of all the epoxy groups of an epoxy resin (a_1), and is compounding all by the range of 0.9-1.1 in the example. (na_2/na_3) receive the na_3 mol number of all the carboxyl groups in dicarboxylic acid (a_3) at this appearance. The ratio of a na_2 mol number of all the carboxyl groups in monocarboxylic acid (a_2) (na_31/na_32) The ratio of a na_31 mol number of all the carboxyl groups in the dicarboxylic acid (a_31) which has 1-6 acryloyl (meta) radicals to the na_32 mol number of all the carboxyl groups in the dicarboxylic acid (a_32) which does not have an acryloyl (meta) radical in dicarboxylic acid (a_3) is shown.

- Molecular weight : Number average molecular weight and weight average molecular weight which were computed by molecular-weight-distribution measurement by polystyrene conversion by GPC (MILLENNIUM32 made from WATERS-J SYSTEM, 40 degrees C of THF solvents).

[0078] The energy-line hardening mold resin constituent for resist ink was prepared by the following presentation about the resin solution (X1-X5, RX1, RX2, RX4) obtained from examples 6-10, five to example of comparison 7 examples 1-5, and the examples 1, 2, and 4 of a comparison.

A resin solution (X1-X5, RX1, RX2 or RX4) The 45 sections Cresol novolak mold epoxy resin (EE214) The ten sections Dipentaerythritol hexaacrylate The four sections IRGACURE 907 (the Ciba-Geigy make, photopolymerization initiator) The 6 section Barium sulfate The 34.5 sections Phthalocyanine Green The 0.5 sections [0079] About each of the <evaluation approach> resin solution (X1-X5, RX1, RX2, RX4), paint and evaluation were performed for the prepared energy-line hardening mold resin constituent for resist ink by the following approaches. A result is shown in the 3rd table and the 4th table.

[0080] (1) It printed and the sample which has the paint film which stated set-to-touch nature 1 each energy-line hardening mold resin constituent for resist ink to the glass epoxy group plate on the screen of 100 meshes, and whose thickness after desiccation is 40 micrometers was obtained, 80 degrees C of this sample estimated the paint film immediately after desiccation for 30 minutes, and the following criteria estimated the tuck nature at the time of finger touch.

O : with no tuck.

** : It is a **** a little [tuck].

x : Those with tuck nature.

[0081] (2) The sample which screen-stenciled like the set-to-touch nature 2 aforementioned set-to-touch nature 1, and was obtained It dries for 30 minutes at 80 degrees C, and, subsequently to a paint film top, is a photo mask :P CW UGRA82 (product made from UGRA) is put. After irradiating the ultraviolet rays of 500 mj/cm² using a high-pressure mercury lamp, the following criteria estimated the tuck generated when exfoliating the step tablet for sensitivity evaluation (product made from KODAKKU step tablet No.2).

O : there is no feeling of a tuck and a step tablet can be exfoliated easily.

** : It is a **** a little [feeling of tuck]. Exfoliation is possible although a step tablet is caught.

x : Those with tuck nature. Into a step tablet, ink adheres and cannot exfoliate easily.

[0082] (3) After leaving the sample which screen-stenciled like the development nature aforementioned set-to-touch nature 1, and was obtained in the 80-degree C oven for 30 minutes and vaporizing a solvent, it was immersed in the sodium carbonate water solution for 60 seconds 1 30-degree C%, and the following criteria estimated the degree which remains on a substrate.

O : the paint film on a substrate does not remain at all.

** : A part of paint film on a substrate remains.

x : The paint film on a substrate does not dissolve but almost remain.

[0083] (4) The sample which screen-stenciled like the sensitometry aforementioned set-to-touch nature 1 of resist ink, and was obtained into a 80-degree C drier, leave it for 30 minutes, vaporize a solvent, and step tablet No.2 (product made from KODAKKU, Inc.) are put on a paint film. After irradiating the ultraviolet rays of 125 mj/cm² and 250 mj/cm², 500 mj/cm² using a high-pressure mercury lamp, it was immersed in the sodium carbonate water solution for 60 seconds 1 30-degree C%, and the step tablet method estimated. The figure of front Naka shows the number of stages of a step tablet, and it is shown that hardenability (sensibility) is excellent, so that a figure is large. On the exposure conditions of 125 mj/cm², five or more steps are success on condition that three or more steps and 500 mj/cm² on condition that one or more steps and 250 mj/cm².

[0084] (5) Leave the sample which screen-stenciled like the definition aforementioned set-to-touch nature 1, and was obtained in a 80-degree C oven for 30 minutes, vaporize a solvent, and it is a photo mask on a paint film :P CW After putting UGRA82 (product made from UGRA) and irradiating the ultraviolet rays of 500 mj/cm² using a high-pressure mercury lamp, it was immersed in the sodium carbonate water solution for 60 seconds 1 30-degree C%, and the minimum value of residual-line width of face and dissolution line breadth estimated.

[0085] (6) The stability test at the time of solvent desiccation (desiccation management width of face) Except having used the tin plate as a substrate, after leaving the sample which screen-stenciled like said set-to-touch nature 1, and was obtained for 50 minutes for 40 minutes for 30 minutes in the 90-degree C oven and vaporizing a solvent, it dipped in the sodium carbonate water solution for 60 seconds 1 30-degree C%, negatives were developed, and viewing estimated the stability at the time of solvent desiccation on the following criteria.

O : the paint film on a substrate does not remain at all.

** : A part of paint film on a substrate remains.

x : The paint film on a substrate does not dissolve but almost remain.

[0086] (7) Except having used the tin plate as a machine physical-properties substrate, after drying the sample which screen-stenciled like said set-to-touch nature 1, and was obtained in a 90-degree C oven for 30 minutes, ultraviolet rays were irradiated two times 500 mj/cm, hardening was performed at 150 more degrees C for 1 hour, it exfoliated from the substrate, the obtained sample was cut to the strip of paper of 7cm length by 1cm width of face, and the hauling trial was performed. Environmental temperature was 53RH% at 23 degrees C. In addition, it was made into 10mm between chucks, and the hauling rate measured by 10 mm/min.

[0087]

[Table 3]

第3表

項 目		実施例				
		7	8	9	10	11
樹脂溶液の名称		X 1	X 2	X 3	X 4	X 5
指触乾燥性 1		○	○	○	○	○
指触乾燥性 2		○	○	○	○	○
現像性		○	○	○	○	○
感度	125mj/cm ² (段)	4	6	6	5	7
	250mj/cm ² (段)	7	10	10	8	12
	500mj/cm ² (段)	10	12	12	9	14
解像性 (μm)		20	20	20	20	20
乾燥 管理幅	30分間乾燥	○	○	○	○	○
	40分間乾燥	○	○	○	○	○
	50分間乾燥	○	○	○	△	○
機械 物性	破断強度 (MPa)	87	75	77	85	90
	破断伸度 (%)	5.9	5.8	5.0	6.2	8.5
	弾性率 (MPa)	1890	1920	1620	1710	1850

[0088]

[Table 4]

第4表

項 目		比較例		
		5	6	7
樹脂溶液の名称		R X 1	R X 2	R X 4
指触乾燥性 1		×	○	○
指触乾燥性 2		×	○	○
現像性		○	×	×
感度	125mj/cm ² (段)	1	—	—
	250mj/cm ² (段)	2	—	—
	500mj/cm ² (段)	4	—	—
解像性 (μm)		40	100<	40
乾燥 管理幅	30分間乾燥	○	×	×
	40分間乾燥	○	×	×
	50分間乾燥	○	×	×
機械 物性	破断強度 (MPa)	65	77	72
	破断伸度 (%)	2.2	6.5	5.3
	弾性率 (MPa)	1850	1490	1580

[0089] The 3rd table shows the evaluation result of the constituent for resists adjusted using the energy-line hardening mold resin solutions X1-X5 compounded in the examples 1-5. Moreover, the 4th table

shows the evaluation result of the constituent for resists adjusted using the energy-line hardening mold resin solutions RX1, RX2, and RX4 compounded in the examples 1, 2, and 4 of a comparison. In addition, in the example 3 of a comparison, since it gelled, evaluation of a constituent was not completed. The constituent of an example showed the result with all good compounds by set-to-touch nature. Moreover, it was a result good also about development nature. Furthermore about sensibility, the level of success was suited. Definition was as a result of [good] 20 micrometers. Moreover, the result in which the development for about 50 minutes or more is possible is obtained also about desiccation management width of face. About machine physical properties, the result of success [ductility] of those with 5% or more and breaking strength, and an elastic modulus is obtained with all constituents. On the other hand, in the example 5 of a comparison in the 4th table showing the result of the example of a comparison, whenever [set-to-touch nature machine physical-properties, especially breaking extension] is bad, and a problem is in use. Moreover, in the example 6 of a comparison, and the example 7 of a comparison, development nature was bad and a pattern was not able to be created.

[0090]

[Effect of the Invention] The energy-line hardening mold resin which the manufacture approach of this invention can be manufactured also under conditions [****], such as reduction of the amount used, such as a halogen system catalyst, and use of a non-halogen system catalyst, is useful to reduction of the halogen system ionicity matter which remains in a paint film, and is moreover excellent in the engine performance fundamental as a constituent for resists, and may improve physical properties, such as toughness, sharply is obtained. Moreover, the energy-line hardening mold resin constituent of this invention using this energy-line hardening mold resin is excellent in tuck nature, development nature, the stability test at the time of solvent desiccation, sensibility, definition, machine physical properties, etc. as a constituent for resists.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The dicarboxylic acid (a3) containing the dicarboxylic acid which has the monocarboxylic acid (a2) and (meta) the acryloyl radical which have 2 functionality epoxy resin (a1) and an acryloyl (meta) radical is used as an indispensable component. The manufacture approach of the energy-line hardening mold resin characterized by making the hydroxyl-group content denaturation epoxy acrylate compound (A) which used at the following formula (1) and a rate in which each (2) is satisfied, was made to react under existence of a catalyst, and was obtained, and an acid anhydride (B) react.

$0.9na1 < na2 + na3 < 1.1na1$ (1)

$0.2 < na2/na3 < 4.0$ (2)

[-- the inside of a formula and na1 -- the mol of all the epoxy groups in an epoxy resin (a1) -- a number and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

[Claim 2] The manufacture approach of energy-line hardening mold resin according to claim 1 that a catalyst is a non-halogen system catalyst.

[Claim 3] The manufacture approach of energy-line hardening mold resin according to claim 1 that a catalyst is a phosphine system catalyst.

[Claim 4] The manufacture approach of the energy-line hardening mold resin according to claim 2 which is dicarboxylic acid with which an epoxy resin (a1) contains the dicarboxylic acid (a31) in which monocarboxylic acid (a2) is an acrylic acid (meta), and dicarboxylic acid (a3) moreover has 1-6 acryloyl (meta) radicals with 2 functionality epoxy resin of 140-250g (g/eq)/Eq of weight per epoxy equivalent.

[Claim 5] The manufacture approach of the energy-line hardening mold resin according to claim 3 which is dicarboxylic acid with which an epoxy resin (a1) contains the dicarboxylic acid (a31) in which monocarboxylic acid (a2) is an acrylic acid (meta), and dicarboxylic acid (a3) moreover has 1-6 acryloyl (meta) radicals with 2 functionality epoxy resin of 140-250g (g/eq)/Eq of weight per epoxy equivalent.

[Claim 6] The manufacture approach of the energy-line hardening mold resin according to claim 4 or 5 which is that in which dicarboxylic acid (a3) contains the dicarboxylic acid (a31) which has 1-6 acryloyl (meta) radicals, and the dicarboxylic acid (a32) which does not have an acryloyl (meta) radical in the range in which the mole ratio (na31/na32) becomes 1-10.

[Claim 7] The manufacture approach of the energy-line hardening mold resin according to claim 4 or 5 which dicarboxylic acid (a31) is dicarboxylic acid which the compound, the tricarboxylic acid anhydride, and/or tetracarboxylic acid 2 anhydride which have an acryloyl (meta) radical and a hydroxyl group are made to react, and is obtained, and is dicarboxylic acid which has 1-6 acryloyl (meta) radicals.

[Claim 8] The manufacture approach of the energy-line hardening mold resin of claim 4 or 5 term publication whose epoxy resins (a1) are the bisphenol mold epoxy resin of 170-250g (g/eq)/Eq of weight per epoxy equivalent, and/or its hydrogenation object.

[Claim 9] The manufacture approach of energy-line hardening mold resin according to claim 4 or 5 of using monocarboxylic acid (a2) and dicarboxylic acid (a3) at a rate in which the following type (2-1) is

satisfied.

$$0.3 < na2/na3 < 3.0 \quad (2-1)$$

[-- the inside of a formula and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

[Claim 10] The dicarboxylic acid (a3) containing the dicarboxylic acid which has the monocarboxylic acid (a2) and (meta) the acryloyl radical which have 2 functionality epoxy resin (a1) and an acryloyl (meta) radical is used as an indispensable component. The hydroxyl-group content denaturation epoxy acrylate compound which used at the following formula (1) and a rate in which each (2) is satisfied, was made to react under existence of a catalyst, and was obtained (A), The energy-line hardening mold resin (I) which the acid anhydride (B) was made to react and was obtained, and the energy-line hardening mold resin constituent characterized by containing an epoxy compound (II).

$$0.9na1 < na2 + na3 < 1.1na1 \quad (1)$$

$$0.2 < na2/na3 < 4.0 \quad (2)$$

[-- the inside of a formula and na1 -- the mol of all the epoxy groups in an epoxy resin (a1) -- a number and na2 -- the mol of all the carboxyl groups in monocarboxylic acid (a2) -- a number and na3 -- the mol of all the carboxyl groups in dicarboxylic acid (a3) -- a number is expressed.] [however,]

[Claim 11] The energy-line hardening mold resin constituent according to claim 10 whose catalyst is a non-halogen system catalyst.

[Claim 12] The energy-line hardening mold resin constituent according to claim 10 whose catalyst is a phosphine system catalyst.

[Claim 13] The energy-line hardening mold resin constituent according to claim 11 which is dicarboxylic acid with which an epoxy resin (a1) contains the dicarboxylic acid (a31) in which monocarboxylic acid (a2) is an acrylic acid (meta), and dicarboxylic acid (a3) moreover has 1-6 acryloyl (meta) radicals with 2 functionality epoxy resin of 140-250g (g/eq)/Eq of weight per epoxy equivalent.

[Translation done.]